

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-007943**

(43)Date of publication of application : **12.01.1999**

(51)Int.Cl.

H01M 4/02

H01M 4/58

H01M 10/40

(21)Application number : **09-162224**

(71)Applicant : **JAPAN STORAGE BATTERY CO  
LTD**

(22)Date of filing : **19.06.1997**

(72)Inventor : **MURAI TETSUYA**

(54) **LITHIUM SECONDARY BATTERY**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a secondary battery with its high discharge capacity and superior cycle characteristic by a carbon material of a negative electrode comprising a scale piece shaped graphite mixed in a graphite powder including a specific rate of boron.

SOLUTION: A discharge capacity can be increased by use of a graphite containing boron.

The content of boron is preferably 0.10 to 40 wt.%. Since there is a manner in which scaly graphite with its superior conductivity exists around a graphite containing boron, these function as a conductive agent, and power collection property of an electrode is improved. As a result, conductivity between adjacent graphite particles even if charging and discharging are repeated, cycle characteristic is improved. A blend rate of the scaly graphite is preferable such that it is 5 to 20 wt.% of a total of the carbon material. As scaly graphite, a molded carbon whose raw material is a natural graphite or coke graphite, for example, can be used.

### LEGAL STATUS

[Date of request for examination] 07.05.2001

[Date of sending the examiner's decision of rejection] 10.06.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lithium secondary battery which improved the quality of the material of a negative electrode.

[0002]

[Description of the Prior Art] In recent years, various amelioration has piled up aiming at large-capacity-izing of a lithium secondary battery, and some amelioration is added also about the quality of the material of the negative electrode which consists of the carbon material. There is a technique indicated by JP,5-251080,A as the example, and this uses the graphite which contained boron in the negative electrode. According to this technique, the outstanding advantage that the amount of occlusion of the lithium ion to a negative electrode increases, and discharge capacity can be raised is acquired.

[0003]

[Problem(s) to be Solved by the Invention] However, on the other hand, the above-mentioned lithium secondary battery was inferior to the cycle property, and had the problem that a life was short. According to research of this invention person, the reason is because it is easy to generate a boron compound with low conductivity in the front face of the graphite containing boron and the contact resistance between graphite powder becomes large. Originally, in this kind of rechargeable battery, when a lithium ion carries out occlusion to a graphite or is emitted to it in connection with that charge and discharge, graphite powder is in the inclination for the graphite which contact nature with adjoining graphite powder falls, and is not related to receipts and payments of a current with the exterior to increase gradually in order to repeat expansion and contraction. However, in the lithium secondary battery which used the conventional boron content graphite, since the surface electrical resistance of a graphite is larger, the contact nature between graphite powder falls at an early stage more, and a cycle property worsens.

[0004] This invention was made in view of the above-mentioned situation, and the purpose is in moreover offering the lithium secondary battery which is excellent also in a cycle property, being able to raise discharge capacity.

[0005]

[Means for Solving the Problem] The lithium secondary battery of claim 1 is a lithium secondary battery make the negative electrode equipped with the carbon material which carries out occlusion of the lithium, and the positive electrode equipped with the lithium compound come to counter through a separator, and said carbon material has the description at the place which comes to mix scale-like graphite powder to the graphite powder containing 0.01 - 40% of the weight of boron.

[0006] The lithium secondary battery of claim 2 has the description at the place which added the scale graphite of the above so that it might become 5 - 20 % of the weight to the whole carbon material.

[0007]

[Function and Effect of the Invention] According to invention of claim 1, discharge capacity can be increased by use of the graphite containing boron. And since it becomes the gestalt to which the scale-

like graphite excellent in conductivity exists in the perimeter of the boron content graphite, these function as an electric conduction agent and the current collection nature of an electrode improves. Consequently, the conductivity between the graphite particles which adjoin even if it repeats charge and discharge is maintained, and a cycle property is improved.

[0008] In addition, it is desirable to use what graphitized the shaping carbon which used a natural graphite or coal, and petroleum coke as the raw material, for example as a scale-like graphite, and to use the artificial graphite which ground these so that mean particle diameter might serve as the shape of a scale which is 5-50 micrometers. It is because the anisotropy in a particle is strong purely [ these / a front face ] and conductivity is high. When the impurity has adhered to the front face, surface conductivity will fall, and it will become the hindrance on a current collection disposition, and an early irreversible capacity will increase.

[0009] Moreover, as a graphite containing boron, the water solution of  $H_3BO_3$  can be added to a graphite, for example, and it can mix, and can manufacture by calcinating this in an inert atmosphere. As a content of boron, 0.001 - 40 % of the weight is suitable, and 0.1 - 15 % of the weight is especially the most desirable.

[0010] Although suitable effectiveness can be acquired if the compounding ratio of a scale-like graphite is 0.1 % of the weight or more, it is desirable to add so that a boron content graphite may become 5 - 20% of the weight of the whole carbon material (invention of claim 2). It is because increase of discharge capacity can be aimed at suppressing increase of irreversible capacity effectively.

[0011]

[Example] Hereafter, some examples of this invention are explained. It mixed at a rate which shows the boron content graphite which is 5 % of the weight, and the scale-like graphite of 15 micrometers of mean diameters in the next table 1, and the boron abundance ratio in a graphite added 10% of polyvinylidene fluoride solution which used N-methyl pyrrolidone as the solvent 5% of the weight to the carbon material, was mixed to it, and the negative-electrode paste was manufactured. The above-mentioned negative-electrode paste was applied so that thickness might become copper foil with a thickness of 30 micrometers with 100 micrometers, it dried at 100 degrees C for 2 hours, this was started so that it might become 2cm angle, it pressed so that porosity might become 25%, and it considered as the negative-electrode plate.

[0012] The above-mentioned negative-electrode plate was made into the operation pole, and the metal lithium was used for the reference pole, for example, it considered as well-known cell structure on both sides of the micropore film separator made from polyethylene, the electrolytic solution (one-mol Li PF<sub>6</sub> / EC+DEC) was poured in here, and the lithium secondary battery was constituted. It is this rechargeable battery 0.2 mA/cm<sup>2</sup> It charged until negative-electrode potential was set to 0V to the metal lithium positive electrode by constant current, it discharged until the potential of a negative electrode was set to 1.5V next, this charge-and-discharge cycle was repeated, and the electrode characteristic was evaluated as shown in degree table.

[0013]

[Table 1]

	鱗片状黒鉛 の配合比 (w t %)	1 サイクル目 放電容量 (mA h / g)	1 サイクル目 不可逆容量 (mA h / g)	20 サイクル後 容量保持率 (%)
比較例 1	0.0	345	38	74
実施例 1	0.1	333	37	89
実施例 2	5	345	35	92
実施例 3	20	342	34	92
実施例 4	50	332	36	92
実施例 5	80	328	38	92
実施例 6	99	325	39	96
比較例 2	100	310	42	97

Here, capacity retention shows the rate of discharge capacity to 1 cycle eye of 20 cycle eye. In the example 1 of a comparison which is not mixing the scale-like graphite, to the capacity retention of 20 cycle eye being 74%, capacity retention is greatly improved with 89 - 96%, and the outstanding cycle property is acquired by the examples 1-6 which made the addition of a scale-like graphite 0.1 - 99 % of the weight to the whole so that clearly from an upper table. In addition, in the example 2 of a comparison which made the compounding ratio of a scale-like graphite 100%, irreversible capacity is not greatly [ as 42 mAh/g ] desirable.

---

[Translation done.]